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Tadasu Kirihaara, et al.

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for : NIOBIUM POWDER, ANODE FOR USE IN SOLID ELECTROLYTIC
CAPACITOR, AND SOLID ELECTROLYTIC CAPACITOR

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Hiroiyuki Sasai , residing at 4-7, Yotsuya, Shinjuku-ku, Tokyo 160-0004

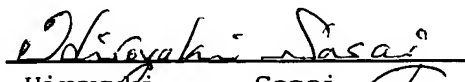
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December 10, 2004

Date


Hiroiyuki Sasai

SPECIFICATION

~~NIOBIUM POWDER, ANODE FOR USE IN SOLID ELECTROLYTIC CAPACITOR,~~
~~AND SOLID ELECTROLYTIC CAPACITOR~~

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Technical Field

The present invention relates to a niobium powder, an anode formed by using the powder, for use in a solid electrolytic capacitor, and a solid electrolytic capacitor
10 formed by using the powder.

Background Art

Although tantalum powder has hitherto been used for electrolytic capacitors, there has been a problem that
15 tantalum is small in production and the supply price of tantalum is unstable. In these years, a trend of using niobium, abundant in amount of deposit and low in supply price, for anodes of electrolytic capacitors has been accelerated. However, electrolytic capacitors using niobium have several
20 drawbacks in comparison with those using tantalum. A primary problem is that the niobium oxide coating film is poor in thermal stability. This causes a problem that the quality is degraded owing to the thermal load applied at the time when the capacitor is mounted as a component, and leakage
25 current is thereby increased.

For the purpose of reducing the leakage current, techniques including a technique of adding nitrogen are available (see for example, the Non-Patent Document 1).

However, these techniques have not been able to be measures that improve the thermal stability.

There has hitherto been available a technique which prepares a niobium powder by reducing niobium pentachloride with hydrogen. In this case, the hydrogen remaining in the niobium powder reaches even a content of 0.7 to 0.8 % by mass. As a powder for use in electrolytic capacitors, the niobium powder brings slightly poor electrostatic capacitance, large leakage current and huge leakage current after application of a thermal load. In this regard, the present inventors have previously provided a niobium powder which contains 1 to 600 ppm of hydrogen and the balance is substantially niobium (see for example, Patent Document 1). Such a niobium is a powder obtained by subjecting the above niobium powder that is prepared by reducing niobium pentachloride with hydrogen, to a thermal treatment, for example, at a temperature of about 1000°C or higher in an atmosphere of Ar. When such a niobium powder is used as an anode of a solid electrolytic capacitor, the capacitor is large in electrostatic capacitance, small in leakage current, and accordingly excellent.

A solid electrolyte capacitor has a structure in which niobium, niobium oxide, a solid electrolyte, graphite, silver and the like are laminated one over another. The solid electrolyte capacitor is fabricated as follows: a niobium powder is sintered at 1000 to 1400°C to produce a porous sintered body, thereafter the porous sintered body is subjected to chemical conversion treatment to form niobium oxide on the surface of the niobium; subsequently the solid

electrolyte layer, the graphite layer and the silver layer are formed; and finally, external terminals are connected.

[Non-patent Document 1] "Metal, vol. 72 (2002), No. 3," (p 221).

5 [Patent Document 1] Specification of Japanese Patent Application No. 2002-11824.

Disclosure of the Invention

The present invention provides a further improved
10 technique described in Patent Document 1. An object of the present invention is the provision of a niobium powder to be used for manufacturing capacitors small in leakage current, small in degradation of leakage current after application of a thermal load, and high in capacitance by enhancing the
15 thermal stability of the oxide coating film of niobium capacitors. Further, another object of the present invention is the provision of anodes, using this niobium powder, for use in solid electrolytic capacitors and solid electrolytic capacitors using this niobium powder.

20 The present invention provides a niobium powder characterized in that the niobium powder includes at least one selected from molybdenum: 0.002 to 20% by mass, chromium: 0.002 to 10% by mass, and tungsten: 0.002 to 20% by mass; and hydrogen: 0.005 to 0.10% by mass, the balance
25 substantially being niobium, and that the specific surface area of the niobium powder is from 1 to 10 m²/g.

It is found that the electrostatic capacitance is enhanced and the leakage current is lowered by limiting the

content of hydrogen in the niobium powder and adding one or more of molybdenum, chromium and tungsten in appropriate contents. The content of hydrogen is appropriately in a range from 0.005 to 0.10% by mass; if the content of hydrogen
5 is either above or below this range, improvement of the electrostatic capacitance and lowering of the leakage current are not found. None of molybdenum, chromium and tungsten is effective when the content thereof is less than 0.002% by mass; when the content of molybdenum or tungsten
10 each exceeds 20% by mass, and when the content of chromium exceeds 10% by mass, the effect is saturated and no further improvement can be found. Molybdenum, chromium and tungsten may be contained each alone or in a combination of two or more thereof. When specific surface area of the niobium
15 powder is either less than $1 \text{ m}^2/\text{g}$ or larger than $10 \text{ m}^2/\text{g}$, the capacitance of a capacitor is lowered, and accordingly, the specific surface area of the niobium powder is set at 1 to $10 \text{ m}^2/\text{g}$.

Moreover, the thermal stability of the niobium oxide
20 coating film is improved when the above described niobium powder contains magnesium: 0.002 to 1% by mass and/or aluminum: 0.002 to 1% by mass.

Additionally, the above described effect of the above described niobium powder is remarkable in powders small in
25 primary particle size; it is preferable that the average particle size of the secondary particles is 10 to $200 \text{ }\mu\text{m}$, which makes it possible to obtain a niobium powder for use in electrolytic capacitors that simultaneously has high

capacitance and low leakage current. Moreover, by regulating the average of the secondary particle sizes so as to be 10 to 200 μm , the moldability can be maintained even when the primary particles are fine particles. Additionally, 5 a niobium powder with the content of hydrogen controlled to an appropriate value makes the boundaries between the secondary particles disappear after pressing and inhibits the edge break of molded bodies. Accordingly, such a niobium powder can improve the moldability as compared to a niobium 10 powder without added hydrogen.

By use of any one of these niobium powders as a raw material, a sintered body is formed as an anode in the interior of a capacitor. A solid electrolytic capacitor in which such an anode is formed comes to have excellent performances in 15 electrostatic capacitance and leakage current properties.

The present invention has made it possible to stabilize the oxide coating film which is important in manufactured capacitors by adding specific components to niobium powders. Consequently, such capacitors can prevent the property 20 degradation caused by mounting as components (reflowing), and additionally, can sufficiently withstand the application of lead-free solder in consideration of environmental issues. Moreover, the stabilization of the coating film has made it possible to manufacture niobium capacitors low in leakage 25 current, high in capacitance and excellent in properties.

Best Mode for Carrying Out the Invention

Preparation of the niobium powders can be carried out by means of a CVD apparatus and the like. A mixture of niobium pentachloride with molybdenum chloride, chromium chloride and tungsten chloride is used as a raw material, and a niobium powder is produced by reducing the mixture with hydrogen. The primary particle size can be controlled to an appropriate diameter by controlling the residence time, the temperature and the like of the raw materials. Further, by carrying out a thermal treatment at about 1000°C in an atmosphere of a non-hydrogen gas such as argon, the secondary particle size and the hydrogen concentration are controlled. An electrolytic capacitor using this niobium powder is excellent in electrostatic capacitance properties and small in leakage current and in the leakage current after application of a thermal load.

Additionally, in the preparation method of a niobium powder, by further adding as raw materials metallic magnesium and metallic aluminum into the interior of the reaction furnace, there can be obtained a niobium powder for use in electrolytic capacitors further smaller in leakage current and in the leakage current after application of a thermal load.

By use of the niobium powders produced as described above, electrolytic capacitors were fabricated as below and the electrostatic capacitance and the leakage current of each of the capacitors were measured. A piece of niobium wire of 0.3 mm in diameter to be used for the anode was embedded in a 0.1 g mass of the niobium powder, and the mass of the niobium

powder was subjected to press molding to a bulk density of 3000 kg/m³. The pellet thus produced was sintered at 1100 to 1400°C in an atmosphere having an internal pressure of the furnace of 1×10^{-3} Pa. The sintered pellet was immersed in
5 a 0.8% by mass aqueous solution of phosphoric acid, a voltage of 20 V was applied for 4 hours to form a chemically converted film on the surface of the niobium, and thus a niobium capacitor as a sample was obtained. Thereafter, in a 40% by mass aqueous solution of sulfuric acid, the capacitance and
10 the leakage current of the niobium capacitor were measured. The leakage current was measured as a value after application of a voltage of 14 V for 5 minutes, and the capacitance was measured as a value at 120 Hz under a condition of an applied bias of 1.5 V.

15 [Examples]

Specific examples of the present invention will be described below with reference to Examples.

[Examples 1 to 5, Comparative Examples 1 to 6]

In the preparation of niobium powders by hydrogen
20 reduction of niobium pentachloride, the components in the niobium powders were varied by varying the addition amounts of molybdenum chloride, chromium chloride, tungsten chloride, metallic aluminum and metallic magnesium. Pellets were fabricated by use of these niobium powders, and then were
25 subjected to the above described treatments. The capacitance and the leakage current (the values under the heading of no thermal load in Table 1) of each of the

capacitors thus obtained were measured. The results thus obtained are shown in Table 1.

[Table 1]

No	Presence/absence of additive components in the niobium raw material						Niobium powder						Niobium capacitor			Remarks		
							Components (% by mass)						Specific surface area (m ² /g)	Average secondary particle size (μm)	Capacitance (μF·V/g)		Leakage current (μA/μF)	
	Molybdenum chloride	Tungsten	Chromium	Aluminum	Magnesium	Molybdenum	Tungsten	Chromium	Hydrogen	Aluminum	Magnesium	No thermal load					After application of a thermal load	
Example 1	Absent	Present	Absent	Absent	Absent	Absent	0.001	4.33	0.001	0.020	0.001	0.001	3.50	43	153000	0.0052	0.0055	
Example 2	Present	Absent	Absent	Present	Present	Absent	0.040	0.001	0.001	0.015	0.005	0.001	5.33	185	184000	0.0043	0.0044	
Example 3	Present	Present	Present	Absent	Present	Present	14.5	0.029	0.035	0.029	0.001	0.80	4.28	79	162000	0.0032	0.0032	
Example 4	Present	Present	Present	Present	Present	Present	0.32	0.007	1.85	0.047	0.015	0.010	3.61	23	157000	0.0029	0.0033	
Example 5	Present	Present	Absent	Present	Present	Present	0.25	0.032	0.001	0.032	0.080	0.16	3.30	142	156000	0.0010	0.0015	
Comp. ex.1	Absent	Absent	Absent	Absent	Absent	Absent	0.001	0.001	0.001	0.015	0.001	0.001	4.03	53	164000	0.0085	0.0794	
Comp. ex.2	Present	Absent	Absent	Absent	Absent	Absent	22.5	0.001	0.001	0.008	0.001	0.001	2.94	28	125000	0.0353	0.0422	
Comp. ex.3	Absent	Absent	Present	Present	Present	Absent	0.001	0.001	13.54	0.095	0.025	0.001	2.82	125	95000	0.0184	0.0584	
Comp. ex.4	Absent	Absent	Absent	Absent	Absent	Absent	0.001	0.001	0.001	0.75	0.001	0.001	3.95	5.7	187000	0.0380	0.0557	No heat treatment of niobium powder

The contents of hydrogen in the niobium powders were measured by means of a thermal conductivity method. The content of molybdenum, the content of tungsten, the content of aluminum, and the content of magnesium in each of the niobium powders were measured by means of the ICP method after pyrolysis in a water bath subsequent to addition of hydrofluoric acid and nitric acid to the niobium powders, and the content of chromium in each of the niobium powders was measured by means of the ICP method after pyrolysis in a water bath subsequent to addition of hydrofluoric acid and sulfuric acid to the niobium powders.

The specific surface areas of the niobium powders were measured by means of the BET method. Moreover, the D_{50} values of the niobium powders were measured by use of a laser particle size distribution analyzer, and the D_{50} values thus obtained were taken as the secondary particle sizes.

As shown in Table 1, in the cases where were used the niobium powders containing at least one selected from molybdenum: 0.002 to 20% by mass, chromium: 0.002 to 10% by mass, and tungsten: 0.002 to 20% by mass; and hydrogen: 0.005 to 0.10% by mass, there were able to be fabricated excellent capacitors large in electrostatic capacitance and low in leakage current.

Moreover, in the cases where were used the niobium powders containing aluminum and magnesium in appropriate contents, there were able to be fabricated capacitors large in electrostatic capacitance and further lower in leakage current.

The samples fabricated as described above and subjected to chemical conversion treatment were then allowed to stand for one hour in a drying furnace heated to 150°C, and thereafter, the leakage currents thereof (the values under the heading of after application of a thermal load in Table 1) were measured. The results obtained are also shown in Table 1. Although in the samples not containing molybdenum, chromium and tungsten, the average of the leakage currents after heating is increased by a factor of about 15 as compared to that before heating, the samples using the niobium powders of the present invention each did not exhibit such a large difference between before and after heating.